

## Determination of Formaldehyde in Maple Sirup: Variation of the Blank

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**The amount of formaldehyde in 23 samples of commercial maple sirup from various parts of the maple-producing areas of the United States ranged from 0.36 to 1.85 ppm with an average of 0.75 ppm. These sirups were made from sap of maple trees not treated with a paraformaldehyde germicidal pellet. This "blank" was lower than the 0.95 value used in the official method for HCHO (31.184-31.189), but the few high values would present a problem for maple sirup producers who must keep residual HCHO in maple sirup below 2 ppm. The distillate of sirup which isolates the formaldehyde yielded 3 carbonyl compound peaks by GLC, one of which corresponded to HCHO. Work is being done to determine if the others may be interfering compounds.**

In obtaining the sweet exudate from the maple tree that is used to make maple sirup, a germicidal pellet of formaldehyde is used to deter bacterial growth in the taphole (1). This treatment releases a small amount of formaldehyde into the sap as it flows out of the tree. Under normal conditions this formaldehyde is lost from the sap during its concentration to sirup by the atmospheric boiling process used. However, a trace of the germicide may remain in the sirup; a maximum tolerance of 2 ppm for this residue has been set by the Food and Drug Administration (2). A method of determining traces of formaldehyde involved was developed for FDA. The Hantzsch reaction of Nash (3) was selected because of its specificity for formaldehyde, its sensitivity, and its relatively simple procedure. The method was adapted to maple sirup and studied collaboratively by 15 laboratories who were potential users of the procedure (4). As a result of the satisfactory accuracy and precision obtained in these analyses, the method is now an official method (5).

During the 1969 maple season an abnormally high amount of residual formaldehyde was found in some samples of sirup. There was no plausible explanation for these values and some studies on the method were initiated by the Associate Referee on Maple Flavors.

An obvious point to check was the *blank* value in the procedure. The maple sirup originally used to determine this value was made by using steam heat, which differs from the usual commercial source of heat, wood or oil. Also, all the sirup thus used was made at one plant, which kept constant several other factors affecting the color and flavor of maple sirup.

For the current work, maple producers in Ohio, Wisconsin, Pennsylvania, Michigan, and New York were asked for samples of sirup produced from trees that had *not* been treated with the germicidal pellets. Twenty-three unpeletted-tree sirups were received, along with an information sheet citing details on the production of the sirup.

The apparent formaldehyde values for these sirups were compared to the established blank value used in the procedure. The data from this study are recorded in Table 1 and can be summarized as follows:

(1) The analytical method was found reliable, but care must be used to follow the procedure as described, especially the distillation step. From suggestions of collaborators, an electric heating mantle was found to improve control of the distillation step.

(2) The formaldehyde value for the 23 samples of sirup from unpeletted trees ranged from 0.36 ppm to 1.85 ppm and averaged 0.75 ppm. The blank correction value prescribed in the method of analysis is 0.90 ppm. Thus, the analyses of these 23 samples indicate a lower natural formaldehyde value than did the samples of the sirup made during the pellet development research. However, the sirup with 1.85 ppm blank value would have shown more than the permissible 2 ppm of residual HCHO with an actual residue of more than 1.05 ppm. More samples are needed to ascertain the frequency of, and perhaps the reason for, the higher level of natural "formaldehyde" in some sirups.

(3) Among the 23 unpeletted samples, the lighter colored sirups tended to have a lower formaldehyde value than the darker ones. The differences were not great. Light amber sirups

**Table 1. Amount of formaldehyde (ppm) in samples of sirup made from sap from unpelleted maple trees**

Sirup Color					
Light Amber		Medium Amber		Dark Amber	
Sample	HCHO	Sample	HCHO	Sample	HCHO
2	0.43	3	0.73	1A	0.36 <sup>a</sup>
11	0.37	12	0.68	4	1.85
14	0.73	13	0.93	19	0.96
15	0.48	18	0.83	28	0.69
16	0.42	20	1.24		
17	0.41	21	0.92		
22	0.72				
23	0.90				
24	0.48				
25	0.77				
26	0.60				
27	0.93				
Range	0.37-0.93		0.68-1.24		0.69-1.85
Av.	0.60		0.90		1.16
Total range	0.36-1.85	Av.	0.75		

<sup>a</sup> Not used as abnormal treatment may have affected color.

averaged 0.60 ppm, medium amber 0.90 ppm, and dark amber 1.16 ppm (due mainly to the 1.85 sample).

(4) Heating a sirup 3 hr at 15 psig in an autoclave (250°F) increased the formaldehyde value. For example, an unheated sirup had a formaldehyde value of 0.45 ppm and a sirup heated as above, 1.50 ppm.

(5) There was no detectable effect of other processing procedures on the formaldehyde value. Some of these variables are (a) collection of sap by bucket or tubing, (b) type of fuel used, (c) type of evaporator used, and (d) method of filtering.

There are carbonyl compounds in maple sirup (6) and therefore a number of such compounds were tested with the acetylacetone reagent of the Nash procedure. Table 2 lists the compounds tested and their reactions.

Of the compounds tested, glyoxal and acetol reacted the same as HCHO; in addition, glyoxal reacted at the same rate and intensity. Acetol is found in maple sirup; glyoxal is not.

To investigate further the compounds from maple sirup that could react with the color reagent, the distillate obtained in the first part of the procedure (isolation of the HCHO) was treated with 2,4-dinitrophenylhydrazine and the hydrazones obtained were analyzed by the GLC

**Table 2. Reaction of carbonyl compounds with acetylacetone (Nash's reagent)**

Compound	Relative Reaction
Formaldehyde	+++ at once
Acetaldehyde	-
Acetol	+ slowly
Methyl glyoxal	++ orange at once
Glyoxal	+++ at once
Glyceraldehyde	-
Hydroxymethylfurfural	-
Glucose	-
Fructose	-

method of Soukup *et al.* (7). Three peaks were obtained, one corresponding to the retention time for formaldehyde 2,4-dinitrophenylhydrazine and the others unknown. The amount of these compounds in the distillate was too small for identification by the mass spectrograph available. Further identification of these compounds will be undertaken as soon as more sensitive equipment (now on order) becomes available.

### Recommendations

In view of the high degree of accuracy needed for the determination of formaldehyde in maple sirup, work should be continued to improve the present official method.

# REFERENCES

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